LEVELS AND PROFILES OF POLYCYCLIC AROMATIC HYDROCARBONS AND POLYCHLORINATED BIPHENYLS IN SOIL AT AN INDUSTRIAL AREA IN DAR ES SALAAM, TANZANIA

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ABSTRACT

This study investigated the levels and profiles of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in soil from an urban/industrial area in Dar es Salaam, Tanzania. Analysis was performed using a high resolution gas chromatograph coupled to a high resolution mass spectrometer (GC–MS). The results indicated that the contents of total PAHs (16 US EPA priority PAHs) ranged from 104 ng/g to 35890 ng/g and the pollution level is classified as a moderate level with some spots of high and very high pollution levels. The composition profiles of PAHs were dominated by high molecular weight (4-6 rings) PAHs. The ratios of phenanthrene/anthracene and fluoranthene/pyrene indicated that the concentrations of PAHs in the area were influenced by pyrogenic (combustion) sources and petrogenic (petroleum) sources. The total concentrations of 18 PCBs in soil varied from 0.4 ng/g to 282 ng/g. Most of the PCBs concentrations were generally low. PCB 138, PCB 153, PCB 180, PCB 101 and PCB 118 accounted largely among the contaminants of PCBs.

KEYWORDS: PAHs, PCBs, Soil, Urban, Tanzania

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are among the classes of persistent organic pollutants (POPs) in the environment. PAHs and PCBs have been documented to cause many environmental and health problems. Some PAHs and their derivations are highly toxic. Their mutagenic or carcinogenic properties are the main risks to human health. Other health effects include liver, thyroid, dermal and ocular changes, reduced birth weight and reproductive toxicity (ATSDR, 1995; ATSDR, 2000). PAHs are by products of combustion and are naturally occurring chemicals in the environment. Forest fires and volcanoes are major natural sources of PAHs, but there are anthropogenic sources as well due to burning of fossil fuels, including automobile and industrial emissions (ATSDR, 1995). The low molecular weight (LMW) PAHs (containing two and three rings) are abundantly produced at low to moderate temperatures, such as wood and coal combustion, while high molecular weight (HMW) PAHs (containing four or more rings) are generated at high temperatures, such as vehicle emission (Mastral and Calle, 2000).

PCBs can be released into the environment from poorly maintained hazardous waste sites that contain PCBs; illegal or improper dumping of PCB wastes; leaks or releases from electrical transformers containing PCBs; and disposal of PCB-containing consumer products into municipal or other landfills not designed to handle hazardous waste. PCBs may also be released into the environment by the burning of some wastes in municipal and industrial incinerators (US EPA, 2013). Once PAHs and PCBs are released into the atmosphere, they are subject to sink in soil via dry and wet deposition. Due to their low vapor pressure, persistence and high octanol/air partition coefficients, they can strongly adsorb to soil organic matter and are likely to be retained for a long time (ATSDR, 2000; Wilcke, 2000). Therefore, soil is an important reservoir for PAHs and PCBs in the environment.

Some studies showed that the levels of POPs such as PAHs in soil correlate with those in the atmosphere, and therefore, their concentrations in soil are usually considered as good indicators of the surrounding pollution (Wilcke, 2000).

The main objective of this study was to investigate the levels and profiles of PAHs and PCBs in soil from an urban/industrialized area in Dar es Salaam, Tanzania. To the best of the author's knowledge, no study has been conducted on such contaminants in soil in Tanzania and therefore, this is the first study.

MATERIALS AND METHODS

Study Area and Sampling

The study area is located at Vingunguti industrial area in Dar es Salaam City. The sampling stations were selected within the area bordered by the main road to the airport on one side (south) and the Central Railway on the other side (north). Soil samples were collected from ten sampling stations located at least 30 m from the road or railway. Surface soils were collected in April 2009 and the sampling depth was 0–10 cm after removal of the litter layer. At each sampling station three samples were taken from different points in a square of 10 m^2 and pooled together to form a composite sample. Each composite sample was wrapped in an aluminium foil and placed in a polyethylene bag. The samples were transported to the laboratory and kept deep frozen at –28 °C until extraction.

Extraction, Clean Up and Analysis

The procedures by Schramm et al. (2008) were adopted with modifications. The samples (5–10 g each) were spiked with labelled internal standards (10 µL of a mixture containing 0.43–1 ng µL^{-1} of all PAHs and PCBs compounds in nonane) and quantitatively extracted by pressurized fluid extraction using an Accelerated Solvent Extractor (ASE 200 Dionex) at a temperature of 120 °C and pressure of 120 bar and with n-hexane: acetone (75:25) as the extraction solvent mixture. Two static cycles of 10 min were applied for a complete extraction. Another sub-sample of each original sample was dried in oven for 24 h at 105 °C and then weighed for dry weight determination. The extracts were passed over anhydrous sodium sulfate to remove water. The extracts were concentrated using vacuum rotary evaporation and the solvent was changed to n-hexane: dichloromethane (1:1) and concentrated to ca.1 mL.

Clean-up of the concentrated extracts was conducted using silica gel (10 g), alumina with 3% H$_2$O (5 g) and anhydrous sodium sulfate (5 g) packed in that order in a glass column (30 cm long and 2.5 cm internal diameter). The extracts were eluted with a mixture of n-hexane and dichloromethane (1:1, 100 mL) and concentrated to 1 mL using a rotary evaporator, then using a very gentle stream of nitrogen to ca. 0.2 mL. The solvent was changed to acetonitrile and concentrated using nitrogen to ca. 0.2 mL. Additional clean-up was performed through a C18 SPE cartridge using C$_{18}$-modified silica gel (1 g), eluted with acetonitrile (5 mL) and concentrated by blowing a gentle stream of nitrogen to ca. 0.2 mL. The concentrated extracts were transferred into clean vials containing recovery standards (20 µL of a 1 ng µL^{-1} solution of ^{13}C-pentachlorotoluene, ^{13}C$_{12}$-1,2,3,4-TCDD and ^{13}C-1,2,3,7,8,9-hexachlorodibenzo-p-dioxin in nonane) and extracts were concentrated with a very gentle flow of nitrogen to 20 µL ready for analytical determination.

Instrumental analysis of the PAHs and PCBs was performed using a high resolution gas chromatograph coupled to a high resolution mass spectrometer (GC–MS). An Agilent 5890 Series II GC equipped with a capillary column (Rtx-CLPesticides 2, 30 m, 0.25 mm ID, 0.2 µm film thickness, Restek) was used. The column temperature programme for PAHs was 60 °C (1.5 min), 10 °C min^{-1} to 225 °C (0 min), 5 °C min^{-1} to 290 °C, 15 °C min^{-1} to 315 °C (20 min) while for PCBs the temperature programme was 100 °C (1.5 min), 3 °C min^{-1} to 270 °C (0 min), 15 °C min^{-1} to 300 °C (10 min). 0.5 µL was injected using an autosampler MPS2 (Gerstel) in pulsed splitless mode by a cold injection system CIS 3

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(Gerstel). The temperature programme for the injector was: 120 °C, 12 °C s^{-1}, 280 °C, 5 min. The carrier gas was helium, head pressure of 16 psi. The temperature at the transferline was 300 °C. The measurements were conducted with a Finnigan MAT 95S mass spectrometer (Thermo) with a resolution of >8000. The ionization mode was EI at 47 eV and 260 °C and the detection was by using the selected ion monitoring (SIM) mode.

The two most intense ions of the molecular ion cluster were monitored for the analytes and labelled standards. The identification of the analytes was performed using retention times, relative retention times and isotope ratios for the labelled standards and respective analytes. The mass fragment with the highest intensity of the molecular ion was used for quantification while the other was used as a ratio mass. All the PAHs and PCBs concentrations were calculated per oven dry weight of soil.

Analytical Quality Assurance and Control

All organic solvents were of picograde quality; anhydrous sodium sulfate and adsorbents were of analytical grade (LGC Promochem, Wesel, Germany). The silica gel was heated overnight at 550 °C. The labelled standards were of over 99% certified purity (Dr. Ehrenstorfer, Augsburg, Germany) and were stored in glass-stoppered flasks or vials in a deep freezer at –28 °C. After use, all glassware and tools were rinsed with a technical mixture of toluene, acetone and hexane, and washed with water and detergent in a washing machine. Thereafter, the glassware was dried in an oven overnight at high temperatures up to 450 °C. Matrix spikes (working standards spiked on sea sand previously dried at 550 °C and mixed with hydromatrix) were prepared, extracted, cleaned and analyzed in parallel with the soil samples. Limits of detection (S/N = 3) ranged from 0.0002 to 0.005 ng/g. The average recoveries in matrix spikes for PAHs and PCBs ranged from 72% to 90%. The coefficients of variation ranged from 6 to 17% for all compounds.

Data Analysis

Graph Pad In Stat software (Motulsky, 1998) was employed to check for the differences in concentrations of PAHs and PCBs among the sampling stations.

RESULTS AND DISCUSSIONS

PAHs and PCBs Concentrations in Soil

The concentrations for the individual PAHs and the total concentrations of 16 PAHs (∑PAHs) for the ten sampling points are presented in Table 1. All 16 PAHs were detected in all the soil samples. The concentrations of total PAHs ranged from 104 ng/g to 35890 ng/g. The PAHs levels are generally similar to those reported in soils in urban and industrialized areas in most studies conducted in other parts of the world, such as Estonia (2200-12300 ng/g), Notre-Dame de Gravenchon industrial area-France (5650±2305 ng/g), Rouen urban-France (2780±879 ng/g), Beijing-China (366 – 27825 ng/g), Tarragona-Spain (281.2–785.5 ng/g) and Dalian-China (650±252–6506±5726 ng/g) (Trapido, 1999; Motelay-Massei et al., 2004; Tang et al., 2005; Nadal et al., 2007; Wang et al., 2007). The PAHs concentrations found in soil in the present study are also comparable to the reported concentrations in sediments and oysters from the inter-tidal areas of Dar es Salaam, Tanzania (78–25,000 ng/g in sediments and 174 – 647 ng/g in oysters) (Gaspare, et al., 2009).

According to the categories from Baumard et al. (1998), ∑PAHs pollution levels are classified into four categories. The pollution levels of ∑PAHs on dry weight basis are: low (0–100 ng/g), moderate (>100–1000 ng/g), high (>1000–5000 ng/g) and very high (>5000 ng/g). In this study ∑PAHs in 80% of the samples could be characterized as moderate pollution levels. The ∑PAHs in soil samples from points A and B could be considered as the pollution levels are high and very high, respectively.

Individual concentrations of PCBs and the total concentrations of 18 PCBs (∑PCBs) in soils of Vingunguti area given according to the different sampling points are shown in Table 2. The sum of PCBs concentrations in soil varied from 0.4 ng/g to 282 ng/g. Most of the PCBs concentrations were generally low except in samples from point B.

In comparison to studies carried out in different industrial and urban areas, the PCBs concentrations of Vingunguti soils are relatively lower than those found in soils from an industrial area in Notre-Dame de Gravenchon-France (∑7PCBs = 150 ng/g) (Motelay-Massei et al., 2004) and in Madrid-Spain (PCBs 32 ng/g) (García-Alonso and Pérez-Pastor, 2003), but are relatively greater than those reported in an urban area in Rouen-France (∑7PCBs = 1.49 ng/g) (Motelay-Massei et al., 2004). Most of the total PCBs concentrations were comparable to those found in soils of a highly industrialized chemical/petrochemical area in Tarragona, Spain (∑7PCBs ranged 0.185–17.895 ng/g with mean values of 4.435–4.673 ng/g) (Nadal et al., 2007), except for point B.

Table 1: PAHs Concentrations in Soil ng/g dw

PAHs	Rings	A	B	C	D	E	F	G	H	I	J
Naphthalene	2	187	2310	63.2	25.1	35	17	80	14.7	26.4	88
Acenaphthylene	3	9.1	217	2	0.75	1.3	1.4	4.4	0.97	0.72	3.5
Acenaphthene	3	9.2	89	2	0.54	1.6	1.6	2.7	0.39	0.5	2.9
Fluorene	3	26	160	4.4	1.3	2.5	2.4	4.9	1.2	0.95	5.2
Phenanthrene	3	318	2715	65.8	27.1	28	17	124	24.4	24.4	65
Anthracene	3	30	334	6.5	1.8	2	1.4	8.8	2.5	1.6	6.8
Fluoranthene	4	96	1322	16	17.2	17	7.2	82	14.8	12.9	37
Pyrene	4	161	1953	30	22.1	12	6	53	10.3	10.2	43
Benzo(a)anthracene	4	28	870	6	13.3	5.8	2	22	5.8	2.8	10
Chrysene	4	155	2568	25.2	14.2	13	7	102	17.1	10.5	34
Benzo(b)fluoranthene	5	42	3862	6.5	11.2	18	6.3	76	14.3	6.1	25
Benzo(k)fluoranthene	5	21	1768	3.9	5.3	6.7	2.1	25	5.4	2.2	11
Benzo(a)pyrene	5	38	4853	6.8	8.9	7.7	3.2	36	6	2.3	14
Dibenzo(a,h)anthracene	5	6	778	1.1	1.5	2.1	2.2	6.9	1.2	0.59	3.6
Indeno(1,2,3-c,d)pyrene	6	67	5464	11.5	9	17	14	49	12.6	4	27
Benzo(g,h,i)perylene	6	113	6627	33.7	12.6	16	13	56	12.1	4.6	42
∑ PAHs	2-6	1306	35890	285	172	186	104	733	144	111	418

A-J = Sampling stations

Table 2: PCBs Concentrations in Soil ng/g dw

PCBs	IUPAC No.	A	B	C	D	E	F	G	H	I	J
Indicator PCB:											
2,4,4'-Trichlorobiphenyl	PCB 28	0.14	2.1	0.16	na	0.03	0.03	0.07	0.2	0.38	0.08
2,2',5,5'-Tetrachlorobiphenyl	PCB 52	0.23	7.3	0.11	na	0.04	0.03	0.09	0.13	0.54	0.15
2,2',4,5,5'-Pentachlorobiphenyl	PCB 101	0.51	23.9	0.23	na	0.05	0.04	0.22	0.14	0.82	0.22
2,2',3,4,4',5'-Hexachlorobiphenyl	PCB 138	1.3	77.9	1.4	na	0.1	0.05	1	0.26	0.76	0.29
2,2',4,4',5,5'-Hexachlorobiphenyl	PCB 153	1.2	48.4	1	na	0.11	0.1	1.1	0.3	0.75	0.29
2,2',3,4,4',5,5'-Heptachlorobiphenyl	PCB 180	1	41.7	3.2	na	0.14	0.06	0.68	0.17	0.58	0.41
Non-ortho PCB:											
3,3',4,4'-Tetrachlorobiphenyl	PCB 77	0.36	18	0.21	na	0.01	0.02	0.56	0.06	0.58	0.1
3,4,4',5-Tetrachlorobiphenyl	PCB 81	0.01	0.31	0.03	na	n.d.	n.d.	0.01	n.d.	0.22	0.02
3,3',4,4',5-Pentachlorobiphenyl	PCB 126	0.01	0.68	0.01	na	n.d.	n.d.	0.01	0.01	0.37	0.03
3,3',4,4',5,5'-Hexachlorobiphenyl	PCB 169	n.d.	0.2	n.d.	na	n.d.	n.d.	n.d.	n.d.	0.11	0.01
Mono-ortho PCB:											
2,3,3',4,4'-Pentachlorobiphenyl	PCB 105	0.3	14.6	0.16	na	0.03	0.02	0.27	0.1	3.1	0.42
2,3,4,4',5-Pentachlorobiphenyl	PCB 114	0.03	7	0.1	na	0	n.d.	0.02	0.01	0.1	0.01
2,3',4,4',5-Pentachlorobiphenyl	PCB 118	0.5	22.7	0.26	na	0.05	0.03	0.45	0.2	1.5	0.3
2',3,4,4',5-Pentachlorobiphenyl	PCB 123	0.02	0.89	0.02	na	n.d.	n.d.	0.02	0.01	0.21	0.02
2,3,3',4,4',5-Hexachlorobiphenyl	PCB 156	0.2	9.2	0.1	na	0.01	0.01	0.18	0.06	0.32	0.04
2,3,3',4,4',5'-Hexachlorobiphenyl	PCB 157	0.04	2.5	n.d.	na	n.d.	n.d.	0.04	0.01	0.03	0.01
2,3',4,4',5,5'-Hexachlorobiphenyl	PCB 167	0.08	3.6	0.1	na	0.01	n.d.	0.09	0.03	0.18	0.02
2,3,3',4,4',5,5'-Heptachlorobiphenyl	PCB 189	0.03	1.1	0.1	na	0.01	n.d.	0.02	0.01	0.02	0.01
∑ PCBs		6.0	282	7.2	na	0.6	0.4	4.83	1.7	10.6	2.43

n.d. = not detected; na = Sample from station D was not analyzed for PCBs.

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PAHs and PCBs Profiles

The composition profiles of PAHs by ring sizes are presented in Figure 1. The profiles were dominated by high molecular weight (4-6 rings) PAHs, which accounted for 49.4-83.8% of the total PAHs concentrations, while low molecular weight (2-3 rings) PAHs accounted for 16.2 – 50.5% of total PAHs concentrations, with average compositions of 62.7% and 37.3%, respectively. LMW PAHs are available to be degraded and easily evaporate into air from soil therefore are subject to transport to other areas from their sources, while HMW species are prone to rapid deposition and retention close to the sources because they are easily adsorbed to the particles and therefore are less lost from soil (Ma et al., 2005).
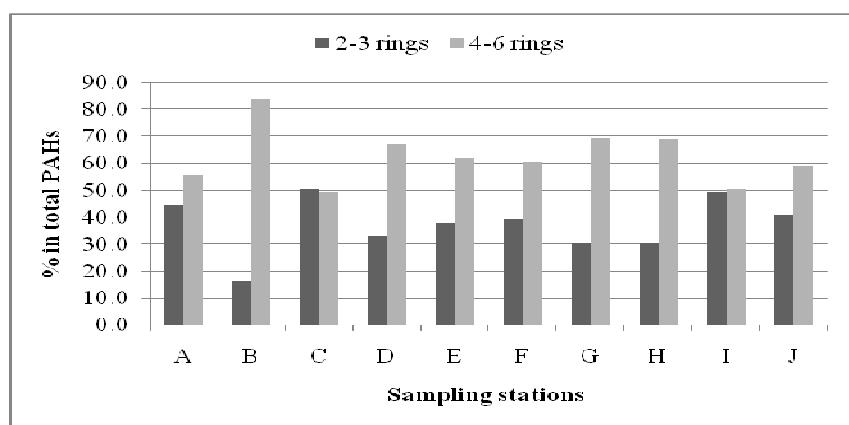

Figure 1: Composition Profile of PAHs in Soil from Vingunguti Industrial Area-Dar es Salaam

The ratios of the PAHs, phenanthrene/anthracene (Phe/An) and fluoranthene/pyrene (Flu/Pyr) are commonly used to distinguish between pyrolytic and petrogenic sources. Phe and An or Flu and Pyr possess similar physico-chemical properties, therefore, variability of the ratios can primarily reflect source characters. Generally, Phe/An ratio > 10 and Flu/Pyr ratio > 1 are characteristic of wood and coal combustion, while Phe/An ratio < 10 and Flu/Pyr ratio < 1 indicate that PAHs mainly come from pyrogenic origin (Yunker et al., 2002). Phe/An ratios vary between 8.1 and 15.3, with 70% of the ratios being > 10 and the Flu/Pyr ratios range from 0.5 to 1.5, with 50% of the ratios above 1 (Table 3), indicating that the concentrations of PAHs in samples were influenced by traffic and industrial emissions as well as wood or biomass combustion within and around the study area.

The congener profile study of PCBs showed that the hexachlorobiphenyl congeners 138 and 153 were the predominant contaminants, followed by heptachlorobiphenyl congener 180 and the pentachlorobiphenyl congeners 101 and 118. Similar profiles have been reported in various studies (Lee et al., 1996; Nadal et al., 2007). In fact, the PCB congeners 138 and 153 have been generally characterized as the most abundant and frequently detected in soils of urban centres and even in forests (Buckland et al., 1998).

The total concentrations of PAHs were significantly greater than those of PCBs (*Mann-Whitney U-statistic = 10.000, U' = 80.000, p = 0.003*) indicating that the area is more affected by combustion activities than activities related to sources of PCBs.

Table 3: Ratios of PAHs

PAHs	A	B	C	D	E	F	G	H	I	J
Phe/An	10.6	8.1	10.1	15.1	14.0	12.1	14.1	9.8	15.3	9.6
Flu/Pyr	0.6	0.7	0.5	0.8	1.4	1.2	1.5	1.4	1.3	0.9

CONCLUSIONS

There were moderate to high levels of pollution by PAHs in the study area. PAHs with four to six rings were more dominant than those with two to three rings. The profiles indicated that the concentrations of PAHs in samples from the study area are related with traffic and industrial emissions as well as wood or biomass combustion. The levels of PCBs were generally low. Indicator PCBs showed the highest concentrations among PCBs congeners.

ACKNOWLEDGEMENTS

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